SOP 24

Calculation of the fugacity of carbon dioxide in pure carbon dioxide gas or in air

1. Scope and field of application

This procedure describes a method for the calculation of the fugacity of carbon dioxide in pure carbon dioxide gas or in air. The fugacity, $f(CO_2)$, is expressed either in Pascals or in atmospheres[1].

2. Definition

The chemical potential (μ_B) of an individual component of a vapor phase can be expressed in terms of its fugacity (f_B). This is defined by the equation

$$RT \ln f_B = \mu_B - \lim_{p \to 0}[\mu_B - RT \ln(x_B p / p°)] \tag{1}$$

where x_B is the mole fraction of B in the gaseous mixture and thus $x_B p$ is the partial pressure of B (p_B) in the vapor phase and $p°$ is a standard pressure (typically 101325 Pa, *i.e.*, 1 atm). The term

$$\lim_{p \to 0}[\mu_B - RT \ln(x_B p / p°)] \tag{2}$$

is thus a standard chemical potential, $\mu_B^°(T)$.

3. Principle

The vapor phase fugacity of either a pure gas ($x_B = 1$) or of a component in a mixture of gases can be calculated from the equation

$$f_B = x_B p \exp\left(\frac{1}{RT} \int_0^p (V_B - RT/p') \, dp' \right). \tag{3}$$

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[1]   1 atm = 101325 Pa.

V_B is obtained from

$$V_B = \left(\frac{\partial V}{\partial n_B} \right)_{T,p} , \tag{4}$$

where V is given by an equation of state for the vapor,

$$V = f(T, p). \tag{5}$$

3.1   The ideal gas equation

The simplest equation of state is the expression for a perfect gas mixture,

$$V = \frac{RT}{p} \sum_B n_B . \tag{6}$$

The integral in equation (3) is then equal to zero and

$$f_B = x_B p . \tag{7}$$

3.2   The virial equation

More generally, the equation of state can be represented by a virial expression,

$$\frac{pV_B}{RT} = 1 + \frac{B(T)}{V_B} + \frac{C(T)}{V_B^2} + \cdots \tag{8}$$

This equation, truncated after the second virial coefficient, is usually adequate to represent p–V–T properties at pressures up to a few atmospheres. It also has the advantage that the coefficient, $B(T)$, can be related to the intermolecular potential energy function of the molecules concerned.

In a mixture of gases,

$$B(T) = \sum_l \sum_m x_l x_m B_{lm}(T) \tag{9}$$

where $B_{lm} = B_{ml}$. The total volume can then be written as

$$V = \sum_k n_k V_k = \sum_k n_k \frac{RT}{p} + \frac{\sum_l \sum_m n_l n_m B_{lm}(T)}{\sum_k n_k} . \tag{10}$$

The partial molar volume of an individual component is

$$V_B = \frac{RT}{p} - \frac{\sum_l \sum_m n_l n_m B_{lm}(T)}{\left(\sum_k n_k \right)^2} + \frac{2 \sum_m n_m B_{Bm}(T)}{\sum_k n_k} \tag{11}$$

and thus

$$V_B = \frac{RT}{p} + \sum_l \sum_m x_l x_m [2B_{Bm}(T) - B_{lm}(T)]p \,. \tag{12}$$

The fugacity is then given by

$$f_B = x_B p \exp\left(\frac{\sum_l \sum_m x_l x_m \left(2B_{Bm}(T) - B_{lm}(T)\right) p}{RT} \right). \tag{13}$$

For a pure gas, this reduces to

$$f_B = p \exp\left(\frac{B_{BB}(T)p}{RT} \right) \tag{14}$$

where $B_{BB}(T)$ is the virial coefficient for the pure gas, B.

A further particular case of equation (13) is the expression for a component of a binary mixture,

$$f_B = x_B p \exp\left[\left(B_{BB}(T) + 2x_C^2 \delta_{B-C}(T) \right) \frac{p}{RT} \right] \tag{15}$$

where

$$\delta_{B-C} = B_{BC} - \tfrac{1}{2}(B_{BB} + B_{CC}) \,. \tag{16}$$

Many of the cross-virial coefficients for the practical computation of fugacity in vapor mixtures have never been measured experimentally. However, a number of empirical approaches can be used.

The simplest of these is the Lewis and Randall rule,

$$f_B = x_B f_B^* \tag{17}$$

where f_B^* is the fugacity of pure component, *B*, at the same temperature and total pressure as the mixture (equation 14).

An alternate method of predicting *B*(*T*), based on statistical–mechanical arguments, is to use the expression

$$B(T) = 2\pi L \int_0^\infty \left[1 - \exp\left(-u(r)/kT \right) \right] r^2 \, dr \tag{18}$$

where *L* is the Avogadro constant and *k* the Bolzmann constant. Here, *u*(*r*)—the pair-interaction energy—is assumed to depend only on the separation, *r*, of the centers of mass of two molecules.

4. Calculation and expression of results

4.1 Virial coefficient of pure carbon dioxide gas

The first virial coefficient of CO_2, $B(CO_2, T)$, is given by the expression (Weiss, 1974) which is based on values reported by Levelt Sengers *et al.* (1971):

$$\frac{B(CO_2, T)}{cm^3\ mol^{-1}} = -1636.75 + 12.0408\left(\frac{T}{K}\right)$$

$$-3.27957 \times 10^{-2}\left(\frac{T}{K}\right)^2 + 3.16528 \times 10^{-5}\left(\frac{T}{K}\right)^3 \tag{19}$$

where $265 < T/K < 320$.

This expression can then be used in equation (14) to calculate the fugacity of pure CO_2 provided that the pressure and temperature of the CO_2 are known.

4.2 Virial coefficient of carbon dioxide in air

In addition, Weiss used the Lennard–Jones (6–12) potential to estimate $u(r)$ and hence calculate values for δ_{BC} for the binary mixture: CO_2–air. He found that the temperature dependence of this parameter is represented by the equation

$$\frac{\delta(CO_2 - air)}{cm^3\ mol^{-1}} = 57.7 - 0.118\left(\frac{T}{K}\right) \tag{20}$$

where $273 < T/K < 313$.

This expression can then be used in equation (15), together with equation (19), to calculate the fugacity of CO_2 in air.

4.3 Example calculations

4.3.1 Fugacity of pure CO_2

$$T = 298.15\ K,$$
$$p = 101.325\ kPa\ (1\ atm).$$

Then,

$$B(T) = -123.2\ cm^3\ mol^{-1},$$

$$f(CO_2) = 101325 \exp\left(\frac{-123.2 \times 10^{-6} \times 101325}{8.31447 \times 298.15}\right)$$

$$= 100.816\ kPa$$

or

$$f(CO_2) = 100.816 / 101.325 = 0.99498\ atm.$$

4.3.2   *Fugacity of CO_2 in air*

$$T = 298.15 \,\text{K},$$
$$p = 101.325 \,\text{kPa} \ (1\,\text{atm}),$$
$$x(CO_2) = 350 \times 10^{-6}.$$

Then,

$$B(T) = -123.2 \ \text{cm}^3 \ \text{mol}^{-1},$$
$$\delta(CO_2\text{–air}) = 22.5 \ \text{cm}^3 \ \text{mol}^{-1},$$
$$f(CO_2) = (350 \times 10^{-6})(101325)$$
$$\times \exp\left\{ \frac{\left[-123.2 \times 10^{-6} + 2(1 - 350 \times 10^{-6})^2 (22.5 \times 10^{-6})\right] \times 101325}{8.31447 \times 298.15} \right\}$$
$$= 35.35 \ \text{Pa} \ (348.9 \times 10^{-6} \ \text{atm}).$$

5.   Bibliography

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